Title of Project : Fabrication and Characterization of Electrical Field – induced Resistive Sensor at the end of Scanning Probe Tip

Grant No.: AOARD-05-4049

PI : Hyunjung Shin, Ph.D.
Name of Organization : Kookmin University, School of Advanced Materials Engineering, Seoul, Korea

1. Measurement and Visualization of Doping Profile in Silicon Using Kelvin Prove Force Microscopy (KPFM) & Scanning Nonlinear Dielectric Microscopy (SNDM)

Scanning resistive probe microscopy (SRPM), a variant of SPM-based techniques, which has a semiconducting resistor at the apex of the tip and can directly observe surface charges, was newly proposed and fabricated. Working principle of detecting surface charge is that resistance changes by field-induced in a small resistive region at the apex of the tip was measured. In order that SRPM technique is a more compatible tool as read/write head of a probe data storage system, higher spatial resolution and sensitivity are needed. A small resistive region at the apex of the tip determines the spatial resolution and sensitivity. Therefore, the measurement of two-dimensional doping profiles in resistive region is of critical importance. For the measurement of two-dimensional doping profiles, KPFM and SNDM are used.

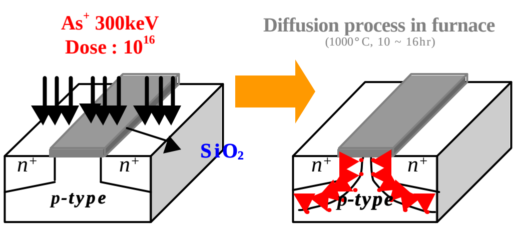


Fig. 1. Schematic diagram of experimental procedure: Ion implantation of As+ ions & annealing process for activation and diffusion of As+ ion at 1000°C for 10~16hr.

Resistive patterns were prepared by following procedure: Doping concentration of the p-type silicon substrate is set at about 1×10^{15}cm^{-3}. A layer of thermal oxides is employed as an implantation mask. Regions of n+ were formed by implanting arsenic ions (1×10^{16}cm^{-2}, 300KeV) and followed by annealing for activation and diffusion of the ions at 1000°C for 10~16hr. During annealing, implanted arsenic ions are diffused into p-Si under the mask where resistive region is formed as shown in Fig. 1 schematically. Prior to KPFM & SNDM measurements, the resistive patterns were exposed by buffered oxide enchant (BOE) to remove surface contaminants as well as thermal oxide layers. The samples were heated for 1h at 150°C to remove the surface water adsorbed layers. SNDM needs high quality oxide for measurement of sample's capacitance. So oxide is grown in H_2O_2 for about 20min.

KPFM is known as a method to locally measure the contact potential difference (CPD) between the tip and the test material's surfaces, thus giving information on the work function of the materials. Doping concentration has been observed by converting work function that exchanged by doping level and type. Surface work function of semiconductor like Si is difficult to analysis quantitatively. Because surface work function is transformed by surface condition - surface state, water layer and so on. On the other hand, in case of SNDM, doping profile was acquired from variation of capacitance. SNDM is a more reproducible technique compared with KPFM because surfaces of desired material are protected with oxide film.

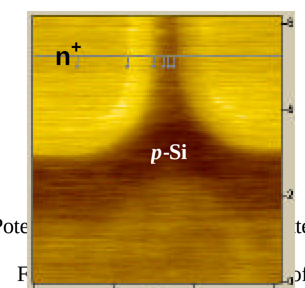


Fig. 2. Pote... tern.

F... of the resistive pattern at equilibrium. It was observed that brighter contrast (higher potential values) in the n+ regions than in the surrounding p regions. In this sample, since doping level in n+-type region (1×10^{19}/cm^3) is much higher than that in the p-type region (1×10^{15}/cm^3), almost all the depletion regions will be formed in the p-Si substrates.

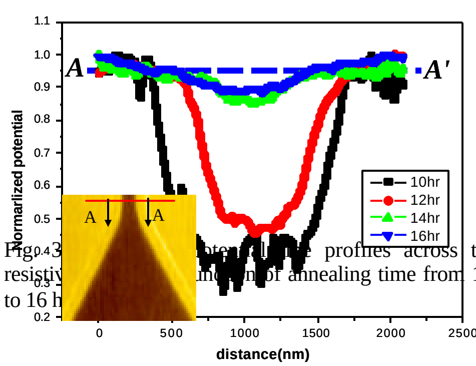


Fig. 3 ... profiles across the resistiv... of annealing time from 10 to 16 h...

Report Documentation Page			*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **27 JUL 2006**	2. REPORT TYPE **Final Report (Technical)**	3. DATES COVERED **18-03-2005 to 18-05-2006**

4. TITLE AND SUBTITLE **Fabrication and Characterization of Electric Field induced Resistive Sensor at the end of Scanning Probe Tip**	5a. CONTRACT NUMBER **FA520905P0350**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Hyun Jung Shin**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Kookmin University,861-1, Jeong Nung Dong, Seo Buk Gu,Seoul 135 - 702,Korea,KE,135-705**	8. PERFORMING ORGANIZATION REPORT NUMBER **AOARD-054049**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **The US Resarch Labolatory, AOARD/AFOSR, Unit 45002, APO, AP, 96337-5002**	10. SPONSOR/MONITOR'S ACRONYM(S) **AOARD/AFOSR**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AOARD-054049**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Fabrication and Characterization of Electrical Field were investigated to develop induced Resistive Sensor at the end of Scanning Probe Tip. The measurement and visual observation of doping profile were performed on Kelvin Prove Force Microscopy (KPFM) & Scanning Nonlinear Dielectric Microscopy (SNDM). NiO Film was fabricated and characterized for Memory Switching applications. Last, effects of Surface Treatment on Work Function & in-plane conductivity of ITO (Indium Tin Oxide) Thin Films were also investigated.

15. SUBJECT TERMS
nanodevices, Scanning Probe Microscopy, Nanostructured materials

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**6**	

Fig. 3 shows normalized potential profiles a cross sectional resistive region (channel) as a function of annealing times from 10 to 16hr. It was clearly indicated that potential differences of n+/p/n+ junction were decreased by increasing annealing time, which implied the implanted arsenic ions are diffused into p-region. Since resistive region (channel) was depleted for 12 hours, thus, we suggested resistive region may be converted into n-type in annealing time of 14 and 16 as shown in Fig. 3. Finally, entire channel was depleted.

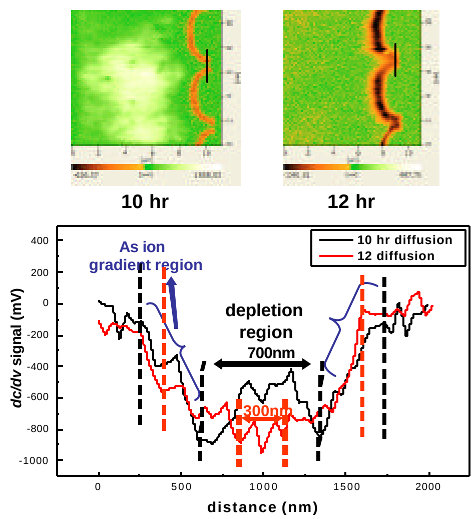


Fig 4. Confirmation of cross sectional resistive region (channel) in 10 hr or 12 hr diffusion sample

In SNDM image, a negative slope of dC/dV in n-type region is observed and a positive slope of dC/dV in p-type region is observed. Doping level in n+-type region is much higher than that in the n-type region and thus dC/dV in n+-type region is lower than that in the n-type region. By variation of capacitance, SNDM image can distinguish doping level and type. Fig 4. shows cross-sectional image and dC/dV signal (mV).

In conclusion, SRPM shows the future possibility as a read/write head of probe storage device because of unique functionality. Prior to the fabrication of resistive probe we have demonstrated the use of KPFM&SNDM for confirmation of cross sectional resistive region (channel).

Publication:

Shin, H., Lee, B-K., Kim, C., Park, H., Min, D.-K., Jung, J., Hong, S., and Kim, S., "Measurement and Visualization of Doping Profile in Silicon using Kelvin Probe Force Microscopy (KPFM)", *Electronic Materials Letters*, **1**[2], 127 - 33 (2005)

Shin, H., Kim, C., Lee, B.-K., Kim, J., Park, H., Min, D.-K., Jung, J., Hong, S., and Kim, S., "Formation and Process Optimization of Scanning Resistive Probe", submitted to *J. Vac. Sci. & Tech. B.,* (2005)

2. NiO Film Memory Switching

Bi-stable memory switching devices based on transition metal oxides (TMO) are now emerging as a candidate for next generation non-volatile memories due to their superior scalability, compatibility with semiconductor processes and low voltage operation. By using conducting atomic force microscopy (C-AFM), we demonstrated the mechanism of forming process and bi-stable memory switching in Pt/NiO/Pt structures. We observed the formation of filamentary current paths in nanometer scale by applying appropriate electric field – called "forming." It is also demonstrated that a few tens of nanometer (10~30nm in diameter) sized filamentary current paths are generated with localized and random fashion by forming process and contribute to the memory switching. In addition, the rupture and reconstruction of the filamentary current paths in random is illustrated after repetitive switching cycle as truly localized phenomena. Also, the filamentary current paths are individually switched with so large distribution of operating voltage and current values are induced by those. To control operating voltage and current we made an artificial filamentary current path using C-AFM. Distribution of current value of high conducting state decreased from 14.74 ± 3.12 mA of Pt/NiO/Pt to 11.92 ± 0.44 mA of Pt/NiO(forming by C-AFM)/Pt as mean values with the standard deviation. Deviation for the operating voltages decreased also from 1.81 ± 0.23 V to 1.76 ± 0.08 V. We successfully demonstrated improved controllability by an artificial filamentary current path. Results validate the feasibility of high density integration by controlling the complete confinement and number density of the filaments.

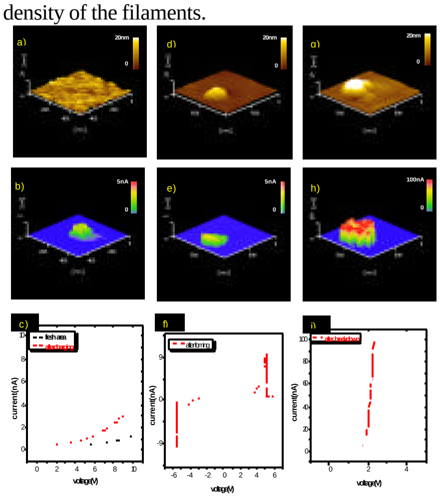


Fig. 1. Change of physical and electrical properties by voltage stress using C-AFM. The topographical images (a, d, g) and current images (b(6V), e(3V), h(3V)) of NiO thin films are shown after the voltage sweep from zero upto 10, 17 and 21V at 10V/s. Local I-V curves in voltage stressed area are observed (c, f, i).

Experimental

Deposition of NiO thin films: Polycrystalline NiO films were deposited on Pt/Ti/SiO2/Si substrates by dc magnetron reactive sputtering methods using Ni targets in an O2 + Ar mixture. Substrate temperature was kept at 300°C, and the working pressure of our chamber was 5mTorr. Sputtering power was 0.27 W/cm2 and flow rates for Ar and Oxygen were 95 sccm and 5 sccm respectively.

Measurements of memory switching behavior using SPA: Resistive memory switching behaviors of our Pt/NiO/Pt structures were measured at room temperature using single-sweep mode of Agilent 4156B semiconductor parameter analyzer on Pt(50 ? x 50 ?)/NiO/Pt structures. The current measurements were performed after each application of bias voltage for 500? . All measurements were done at room temperature and atmospheric pressure. Also, we formed photo resists (PR) patterns with the square opening of 50×50? on NiO/Pt and then applied bias using C-AFM. In subsequent, top electrode of Pt with the thickness of about 100 nm is deposited on the surface of PR patterns with the square opening, and patterned the top electrode through the lift-off process in order to obtain I-V curve of Pt/NiO(stress by C-AFM)/Pt structures using SPA.

Measurements of C-AFM: We use a C-AFM (SPA 400, SEIKO) in contact mode for local measurement. The conductive tips, Au coated Si tip (spring constant of 0.14N/nm) and Br doped conductive diamond coated Si tip (spring constant of 2.8N/nm), were grounded and a voltage was applied across the bottom electrode. Scanning speed was set to 1 Hz, and the applied force between the AFM tip and the surface was between 0.14 nN and 28nN. The detection range of the current for C-AFM was from 10pA to 100nA and the range of applied voltage was from 1V to 100V by a voltage amplifier.

3. Effects of Surface Treatment on Work Function & in-plane conductivity of ITO (Indium Tin Oxide) Thin Films

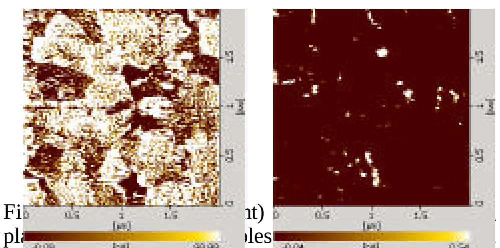
Indium-Tin-Oxide (ITO) is a truly interesting material having good electrical conductivity and high optical transparency in the visible range. Recently, OLEDs have become attractive for full-color displays, and thin films of ITO in OLEDs have been used as anodes for hole injection, due to its unique properties. For the hole injection, work function of ITO is of paramount importance. The work function of ITO films was increased by the surface treatment, and this helps to inject holes more efficiently into the active light-emitting layer from ITO electrodes.

In the present work, the changes of work function and in-plane conductivity of ITO films after CF_4/O_2 plasma treatment by using ICP (inductively coupled plasma) has been studied by C-AFM (Conducting Atomic Force Microscopy), local I-V measurements and KPFM (Kelvin Probe Force Microscopy).

ITO thin films on glass substrates were purchased from Samsung Corning Co. (thickness of 185nm and sheet resistance of 10O/?). Samples were cleaned sequentially by using acetone, IPA (isopropyl alcohol), and DI (deionized) water in ultrasonics for 10min and then dried with high-purity nitrogen gas. The samples were analyzed after the primary cleaning (termed "as-received" sample) and after CF4/O2 plasma treatment in an ICP chamber (termed "plasma-treated" sample), respectively. CF_4/O_2 plasma was generated by a 150W R.F. power supply at 200-mTorr pressure. To activate fluorine ions, a small amount of oxygen was added. The plasma treatments were conducted under two different types of applied bias (20W and no bias) for 3 min, respectively.

C-AFM was performed by Si cantilevers with a spring constant of 11.5N/m, coated with Pt. In the C-AFM measurements, an applied dc bias of 0.1 volt and a contact force of 5.6 nN was applied.

KPFM measurements were made by using a $PtIr_5$-coated Si cantilever with a resonance frequency of 75 kHz and a force constant of ~2.8 N/m. The ac voltage applied to the cantilever was 0.5 volt at frequency 17 kHz.



Fi[illegible] nt) pl[illegible] les the tip was grounded.

Fig. 1 shows as-received (sample A) and plasma-treated (sample B) sample's current images by C-AFM, respectively. In the current images obtained by using C-AFM, conducting and non-conducting regions are observed samples. Most regions of sample A became conducting. However, after CF_4/O_2 plasma treatment, most of sample B became non-conducting. In local I-V measurements, conducting regions of sample A showed ohmic-like behavior. Interestingly, however, most of sample B showed Schottky-like behavior. The Schottky-like behavior in sample B is due to the formation of depletion layers in the ITO thin films. When F ions with strong electronegativity are adsorbed onto the surface of ITO thin films they lead to depletion of electrons from the surface. As a result, the depletion of the electrons causes the band to be bent upward, thus decreasing the in-plain conductivity of ITO thin films.

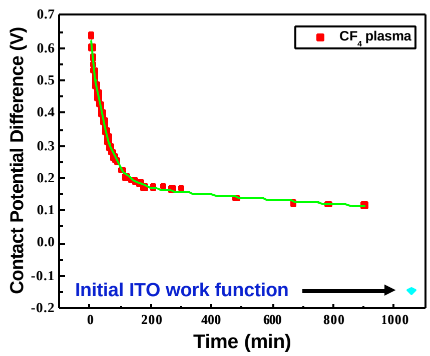


Fig. 2. When exposed in ambient, time evolution of ITO work function

To determine the work function of ITO, KPFM was used. Just after CF4 plasma treatment, the work function of ITO is increased by ~ 0.8 eV. Fig. 2 is shows time evolution of ITO work function during exposure in ambient. Negatively charged ions (F- ions) adsorbed on surface by CF_4 plasma treatment will repel electrons from the surface into the bulk, leading to depletion of electrons from the surface of ITO. When ITO films are exposed in ambient, water absorption on the ITO surfaces is thought to occur. Then, adsorbed water molecules react with fluorine ions which bond to the ITO surface. Therefore, these water molecules could form HF, which is volatile. As HF was gradually desorbed, the work function returned to its initial value.

Surface analysis of ITO thin films before and after CF4 plasma treatment was investigated by using C-AFM and KPFM. CF_4 plasma treatment can modify the ITO surface through introducing F-ions onto the ITO surface. The modification led to an increased surface work function of ITO films, due to the strong electronegativity of fluorine ions. When exposed in ambient, water-molecule adsorption on ITO surfaces led to a reduction of ITO work function. Our results are of importance to improve performance of organic light-emitting diodes (OLEDs), since surface treatments of ITO films as hole–injecting layers can be done effectively.

Publication :
H. Shin, C. Kim, C. Bae, J. Lee, and S. Kim, "Effects of ion damage on the surface of ITO films during plasma treatment", submitted to APL (2006)

4. Future work

The ability of this resistive probe to directly detect charges on solid surfaces also has potential for biological applications such as immuno-diagnostics, DNA-diagnostics, proteomics, and genomics. Detection methods for identifying biological molecules (e.g., nucleic acids, proteins) involves radioisotopic detection, fluorescent labeling, and nanoparticle tagging of the analyte; detection techniques without using these tags still remain attractive. Label-free detection makes it possible to simplify sample preparation, to cut down assay cost, and to eliminate potential artifacts from labeling materials. In this context, our resistive probe could provide a new avenue to direct, label-free detection on biomolecules.

Proteins consisting of amino acids have some charges within their unique structures either in water or in suitable solutions, as amino acids are protonated. Information on position of charges in proteins can be understood their structures and thus their function in biological systems.

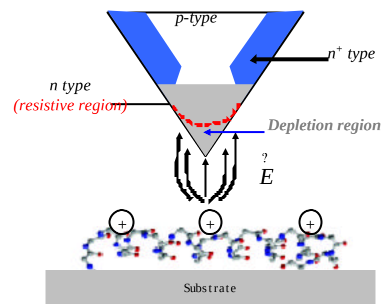


Fig. 1. Schematic illustration of principle of charge detection by using resistive probe.

Fig. 1 shows the detection mechanism, in which the charge on biomolecules perturbs resistivity of resistive region of the probe.

With this local probe with small transistor, single molecular detection is possible without conventional optical, fluorescent means. Detection of DNA single strand can achieve the DNA-diagnostics or the decoding of DNA sequences.

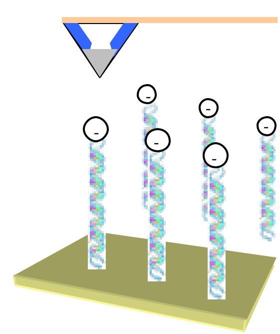


Fig. 2. Schematic illustration of single molecule detection by using resistive probe.

Single arrays can be made in site specific manner using modified contact area lithography (CAL). Gold surfaces can periodically be modified with thiolate self-assembled monolayers; opened holes of gold can also be covered with thiolate DNA molecules. For each of the DNA, the resistive probe functions by sensing the charge at the end of DNA. Furthermore DNA molecules with specific sequences can be identified through biding with corresponding, immobilized DNA; DNA-diagnostics are possible without any perturbations of labeling materials.